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ON THE VOLUME INCREASE DURING CYCLIZATION

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By the division of molar volumes into three constituent volumes, it is demonstrated that the widely observed volume increase during the cyclization is mainly caused by the thermal expansion volume difference in open chain and ring structure.

The pressure effects on reaction rates and equilibrium constants provide activation and reaction volumes respectively and they have been used, along with molar volume measurements, to investigate a wide variety of problems, such as transition state structure, tunnelling effect, hydrophobic interaction and so on[1]. The relations between structural changes, e. g., bond formation, and their effects on the volume of the system were derived from the data obtained so far[1,2]. However, the understanding of the reasons for the observed relations is not necessarily satisfactory. One of such structural changes is cyclization.

It has long been recognized that cyclization causes a characteristic increase in volume as exemplified by the following pure liquid reactions.

$$2CH_2{=}CH(CH_2)_3CH_3 \xrightarrow[\Delta V=-29\,cm^3/mol]{} CH_2{=}CH(CH_2)_9CH_3 \qquad (1)$$

$$CH_2{=}CH(CH_2)_3CH_3 \xrightarrow[\Delta V=-17\,cm^3/mol]{} cy\text{-}C_6H_{12} \qquad (2)$$

In both reactions, one carbon-carbon π bond is converted to a σ bond. However, the volume decrease is more than 10 cm^3/mol smaller for the latter at room temperature. Similar examples were collected by Weale[3]. He also demonstrated that the situation holds in solution as well. For example, at room temperature, methylene group occupies about 16 cm^3/mol in a straight chain solute, but when cyclopentane is dissolved, its partial molar volume reaches to 95 cm^3/mol. Similar observations were made in high pressure reactions. Thus the keto/enol equilibrium constant of ethyl acetoacetate increased with pressure[4] indicating the larger molar volume for the enol form despite the existence of a hydrogen bond. Other examples were listed by Kohnstam[5] and there seems to be little doubt about the reality of the characteristic volume increase, or less negative volume change, during cyclization. The most frequently claimed reason for this phenomenon is the empty space in the center of the ring which is

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1) T. Asano and W. J. le Noble, *Chem. Rev.*, **78**, 407 (1978) and papers cited therein
2) W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1967)
3) K. E. Weale, "Chemical Reactions at High Pressures", E. and F. N. Spon, London, 1967
4) W. J. le Noble, *J. Am. Chem. Soc.*, **82**, 5253 (1960)
5) G. Kohnstam, *Prog. React. Kinet.*, **5**, 335 (1970)

not accessible to the neighbouring molecules[2~6]. Weale[3] also suggested 'free' volume as causative of the observed volume difference without any detailed discussion.

Some years ago the present author and le Noble proposed to divide molar volumes into three constituent volumes in order to analyze reaction and activation volumes[7]. The three volumes are van der Waals volume, V_W, void volume, V_V, and (thermal) expansion volume, V_E. Molar volume at T K, V_T is given by eq. 3.

$$V_T = V_W + V_V + V_E \tag{3}$$

Values of V_W, the volume occupied by the van der Waals spheres have been calculated by several people and Bondi[8] tabulated group contributions to V_W for a variety of atoms and atomic groups. Void volume is the volume of the empty space which inevitably exists amongst the van der Waals spheres and may be considered equal to the difference between zero-point volume of the liquid and its van der Waals volume.

$$V_V = V_0 - V_W \tag{4}$$

Zero-point volume, V_0, is the volume of the hypothetical liquid at 0 K and it can be estimated by Miller's method[9].

If there is an empty space in the center of a cyclic compound and it is responsible for the observed smaller volume decrease in cyclization, it must appear in the void volume change. Therefore, the analysis was performed for several pure liquid reactions including hypothetical cyclizations of polymethylene to cycloalkanes and the results are presented in Table 1.

Table 1 Changes in constituent volumes during pure liquid reactions at 25°C (cm³/mol)

Reaction	ΔV_T	ΔV_W	ΔV_V	ΔV_E
2(1-hexene) ——→ 1-dodecene	−28.8	−3.4	−8.9	−16.5
1-hexene ——→ cyclohexane	−17.2	−4.5	−5.9	−6.7
pentamethylene[a] ——→ cyclopentane	+16.0	−1.1	+3.4	+13.8
hexamethylene[a] ——→ cyclohexane	+14.4	−1.1	+2.3	+13.2

a) The constituent volumes for polymethylenes were estimated from the average volume increments for the processes pentane → hexane and hexane → heptane.

It is obvious that the largest change occurs not in the void volume but in the expansion volume for the hypothetical cyclizations. The void volume increase amounts only to a few cm³/mol indicating that the newly formed empty space in the center of the ring is too small to account for the large total volume increase. Similarly, the reaction volumes for the fiirst two reactions indicate the importance of the expansion volume change. The void volume change is more negative for the dimerization but only by 3 cm³/mol. Most of the ΔV_T difference results from the expansion volume changes.

6) E. Whalley, *Adv. Phys. Org. Chem.*, **2**, 93 (1964)
7) T. Asano and W. J. le Noble, *This Journal*, **43**, 32 (1973)
8) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964)
9) A. A. Miller, *J. Polym. Sci. A-2*, **4**, 415 (1966)

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Further indirect but clear evidence for the major role played by the expansion volume can be obtained from calculation of the empty volume in the center of a cyclic compound. This calculation was performed for cyclohexane assuming that the van der Waals radii for hydrogen and carbon are 1.20 and 1.70 Å respectively[8]. The obtained value for the empty space inside the hexagonal column which is defined by the six carbon atoms and encloses one third of each axial hydrogen[10] is 3.5 cm^3/mol and if we assume the existence of two hydrogen atoms, one on the top and the other at the bottom of the molecule, occupying the space in the center of the three axial hydrogens, there is only 2.6 cm^3/mol void space left inside. The fact that these values are in reasonable agreement with the void volume change difference for the first two reactions in Table 1 provides another support for the use of Miller's zero-point volume in the estimation of the void and the expansion volumes.

Judging from these results, it seems reasonable to conclude that the empty space in the center of a molecule is not large enough to explain the volume difference between ring- and chain-forms.

Now we are in a position to consider the reasons for the larger ΔV_E in the cyclization. Since V_E is the volume obtained by thermal motions, it depends primarily on the degree of freedom. A decrease in the freedom of motion results in a decrease of V_E. In the dimerization of 1-hexene, two molecules are combined together. Therefore, the degree of freedom is expected to decrease more than in its cyclization. Although quantitative discussion is not possible, it may be noted that translational freedom decrease is zero in the cyclization but three in the dimerization. This problem of freedom of motion may be the largest reason for the less negative expansion volume change in the cyclization. However, another factor might play a minor role; the surface area of molecules. The intermolecular forces in nonpolar compounds are proportional to their surface areas. A decrese in the surface area causes a molar volume increase. For example, one mole of neopentane occupies 7 cm^3 more than *n*-pentane and it is entirely caused by the expansion volume[7]. Since cyclohexane is closer to a sphere in its shape than 1-dodecene, a similar effect might be operative, however, the magnitude of this effect can not be estimated at this stage.

To summarize, the main reason for the volume difference between ring and chain structures is not the presence of an empty space in the center of a ring but, at least in nonpolar molecules, larger expansion volume claimed by cyclic structure.

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10) The volume of this hexagonal column itself is 16.87 cm^3/mol.